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Modification of Davidson's Method for the Calculation of Eigenvalues and Eigenvectors of Large Real-Symmetric Matrices: "Root Homing Procedure"

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Davidson's method for the iterative calculation of eigenvalues of large, real-symmetric matrices which makes possible the direct determination of higher roots without knowledge of the exact lower ones is modified to yield just such roots whose eigenvectors have a desired structure, that is, a desired set of dominant components. The algorithm is treated theoretically and applied to some configurational interaction (CI) problems. A study of the convergence behavior of Davidson's scheme is carried out.

1. INTRODUCTION

Large-scale configuration interaction (CI) calculations of electronic wavefunctions of atoms and molecules require the construction of a few of the lowest eigenvalues and their corresponding eigenvectors of large, sparse, real-symmetric matrices. The first method which made the solution of that task practicable for matrices whose dimension gets to the order in magnitude of 10,000 is the root-shifting optimal relaxation (MOR) procedure developed by Shavitt, Bender, Pipano and Hosteny [1]. The following decisive attributes of their scheme make it superior to conventional matrix diagonalization methods:

(a) No arithmetic operations are performed with zero matrix elements which make up usually about 70 per cent of the elements of CI matrices.

(b) The expense of arithmetic operations increases only with $N_{\text{eff}}^2 \cdot I$ where N_{eff} is the "effective" order of the matrix (being much smaller than the actual order because of the zero elements) and I is the number of iterations needed to achieve convergence for all eigenvectors sought.

(c) The matrix which is too big to fit in the computer's central memory can be easily handled in pieces: the elements of only one row (actually only A_{ik} with $i \leqslant k$) are needed at a time, different rows are needed in sequential order.

However, the scheme has several disadvantages: the convergence slows down considerably when the first component of a pair of near-degenerate eigenvalues is treated. Furthermore, the MOR scheme requires a large amount of central memory if several eigenvectors are calculated and it must always find all eigenvalues below the one desired.

Recently Davidson [2] proposed a new method to handle such large CI matrices. His scheme has the same advantages as the MOR method, but overcomes all disadvantages of the latter: the convergence is not hindered in the case of near-degeneracy of roots. In addition it provides the possibility to calculate a distinct root without finding exact solutions for any lower ones.

The direct calculation of a higher root with that scheme is, however, affected by the following problem: to start the Davidson procedure for the kth root a vector subspace of the order l with $l \geqslant k$ is needed which contains in the ideal case good approximations for the first k exact eigenvectors. In practice such a subspace is obtained by a prediagonalization of an appropriate submatrix. However, the resulting trial vectors do not, in general, reflect the ordering of the first k eigenvectors of the full problem. Hence, one cannot take full advantage of that very attractive features of Davidson's method to calculate a certain root directly.

Therefore, a modification of Davidson's algorithm is proposed in the present paper. The modified scheme directs the convergence to one or several desired roots. That is, in spite of a possible occurrence of root inversion the modified procedure enforces convergence to just such eigenvalues whose eigenvectors have a desired structure.

In the present paper this "root-homing procedure" (RHP) is discussed in detail. A theoretical investigation of the convergence of the Davidson method is performed also. Finally, test calculations are reported and an application to actual CI methods is discussed.

2. Davidson's Method

The determination of the kth eigenvalue and of the corresponding eigenvector $\mathbf{x}_k$ is established in Davidson's algorithm by the following procedure: the eigenvector $\mathbf{x}_k$ is iteratively expanded in an orthonormal vector basis. In the Mth approximation $\mathbf{x}_k$ is:

$$\mathbf{x}_k^{(M)} = \sum_{j=1}^{l} \alpha_{j,k}^{(M)} \mathbf{b}_j^{(0)} + \sum_{j=l+1}^{M} \alpha_{j,k}^{(M)} \mathbf{b}_j^{(k)} \tag{1}$$

The first l expansion vectors $\mathbf{b}_j^{(0)}$ define the zero-order subspace. The vectors $\mathbf{b}_{l+1}^{(k)}, \ldots, \mathbf{b}_M^{(k)}$ are obtained in $M - l$ subsequent iterations. They are determined as to give a fast convergence of the expansion (1). The superscript k in $\mathbf{b}_j^{(k)}$ indicates

the dependence of the expansion vectors on the eigenvalue number. The expansion coefficients $\alpha_{j,k}^{(M)}$ in (1) are the components of the kth eigenvector of the matrix $(\tilde{a}_{ij})$ of the order M which is defined by

$$\tilde{a}_{ij} = (\mathbf{b}_i^{(m)}, \mathbf{A}\mathbf{b}_j^{(m')}) \qquad \text{with} \quad \begin{matrix} m, m' = 0; i \leqslant l, j \leqslant l \\ = k; i > l, j > l \\ i, j = 1, 2, \ldots, M. \end{matrix}$$

The eigenvalue $\lambda_k^{(M)}$ of $(\tilde{a}_{ij})$ provides an upper bound for the kth eigenvalue of the full secular equation.

In the following iteration step the vector $\mathbf{b}_{M+1}^{(k)}$ is obtained by Schmidt-orthogonalization of the vector $\mathbf{d}_{M+1}^{(k)}$ to all M expansion vectors already present. $\mathbf{d}_{M+1}^{(k)}$ is defined by

$$\mathbf{d}_{M+1}^{(k)} = \mathbf{D} \cdot \mathbf{q}_{M+1}^{(k)} \tag{2}$$

with

$$D_{n,m} = \delta_{n,m}/(\lambda_k^{(M)} - A_{nm})$$

$$\mathbf{q}_{M+1}^{(k)} = (\mathbf{A} - \lambda_k^{(M)}\mathbf{1})\, \mathbf{x}_k^{(M)}$$

Convergence is achieved if $|\, \mathbf{q}_M^{(k)} \,|$ becomes less than a given appropriate threshold.

To calculate a further root the vectors

$$\mathbf{x}_r^{(M)} = \sum_{j=1}^{l} \alpha_{j,r}^{(M)} \mathbf{b}_j^{(0)} + \sum_{j=l+1}^{M} \alpha_{j,r}^{(M)} \mathbf{b}_j^{(k)}, \qquad r = 1, 2, \ldots, l$$

are taken as the new according to the Hylleraas–Undheim theorem [5] *improved* starting subspace where M is the final dimension of the expansion (1) for the vector just finished. This implicit improvement of the cases still to be done is another feature which makes the Davidson method superior to the MOR scheme.

The dimension of the submatrix $(\tilde{a}_{ij})$ which is diagonalized by conventional standard methods increases by one in each itereation step ($M \to M + 1$). In the limiting case $M \to N$ where N is the dimension of the full secular equation all eigenvalues of $(\tilde{a}_{ij})$ are identical to the eigenvalues of the full problem.

But in practice convergence is achieved after few iterations ($M \ll N$). In the case of a nonideal starting subspace the roots of $(\tilde{a}_{ij})$ so obtained need not necessarily have the same eigenvalue ordering, as the corresponding ones in the full problem (see Section 5, Table I, III) nor need the eventually existing "eigenvalue holes" in the subspace be filled up completely. That means that even if the eigenvalue number k of a desired root of the full secular equation were known the use of the latter as a k value in the procedure described above would not guarantee convergence of $\lambda_k^{(M)}$ to the right root.

The sequential calculation of a series of roots until finding the one sought would be one way to overcome this difficulty. The fewer total number of iterations needed would be the only advantage over the MOR method.

TABLE I

Iteration Steps Needed for the Direct Determination of the Sixth Root of the Ethene Matrix without Using Prediagonalization Results[a]

M	$\lambda_k^{(M)}$	$\mid q_M \mid$	k
1	−78.59767227	0.6222497	1
2	−78.76023843	0.1356590	1
3	−78.76906250	0.1067663	1
4	−78.85120680	0.2442999	1
5	−78.77303221	0.1802442	2
6	−78.77366252	0.2884035	2
7	−78.90292513	0.2122264	2
8	−78.77077014	0.0341811	3
9	−78.77194205	0.0568409	3
10	−78.80793335	0.1031651	3
11	−78.77117318	0.0062123	4
12	−78.77120029	0.0017138	4
13	−78.77120253	0.0006209	4
14	−78.77120277	0.0001997	4
15	−78.81420173	0.0384177	4
16	−78.77120273	0.0002237	5
17	−78.77120277	0.0000676	5
18	−78.77120278	0.0000214	5
19	−78.77120278	0.0000807	5
20	−78.80616454	0.0787059	5
21	−78.77120278	0.0000074	6
22	−78.77120278	0.0000085	6
23	−78.77120278	0.0000074	6
24	−78.77120278	0.0000032	6
25	−78.77120278	0.0000008	6

[a] Nonzero coefficient of the starting vector: 1.0 in position 14 (see Table II).

Notation: M, dimension of the submatrix $(\tilde{a}_{ij})$; $\lambda_k^{(M)}$, kth eigenvalue of $(\tilde{a}_{ij})$; k, currently treated root number; $\mid q_M \mid$. convergence criterion.

TABLE II

Comparison of the Exact Lowest Five Roots and the Main Components of Their Eigenvectors with Their Approximative Counterparts Resulting as By-products from the Direct Calculation of the Sixth Root of the Ethene Matrix[a]

Root	E[a.u.]	E'[a.u.]	MC	MC'
1	−78.991677	−78.983687	0.964655 (1)	0.966134 (1)
				0.065371 (13)
2	−78.937455	−78.936687	0.965219 (13)	0.068738 (1)
				0.964174 (13)
3	−78.847371	−78.843086	0.965378 (11)	0.965405 (11)
			0.125004 (12)	−0.050936 (12)
			0.090101 (125)	0.161302 (125)
			0.068596 (389)	−0.059589 (147)
			0.087278 (393)	0.052934 (389)
			−0.071098 (406)	0.079686 (393)
				−0.076895 (406)
4	−78.814648	−78.814529	0.162298 (14)	0.162727 (14)
			0.684251 (144)	0.714605 (144)
			0.693114 (147)	0.662254 (147)
			0.065022 (601)	0.067545 (601)
			0.065830 (645)	0.062553 (645)
5	−78.812900	−78.812452	−0.067242 (11)	−0.076313 (11)
			0.702490 (144)	0.672231 (144)
			−0.693678 (147)	−0.723188 (147)
			0.064581 (601)	0.058218 (601)
			−0.063713 (645)	−0.064711 (645)
6	−78.771203	—	0.939046 (14)	—
		—	0.057617 (16)	—
		—	−0.122485 (144)	—
		—	0.057840 (145)	—
		—	−0.122437 (147)	—
		—	0.057855 (149)	—

[a] E, E', exact and approximate energies; MC, MC', exact and approximate main components for the CI-vectors. The integers in parenthesis specify their positions.

But if one does not keep the eigenvalue number k of $(\tilde{a}_{ij})$ fixed but lets it assume a value which is adapted to an eventually new situation in the subspace arising in a further iteration step it is, in fact, possible to calculate directly one or several roots whose eigenvectors have a desired structure. The corresponding modification of Davidson's method which makes it possible to use the latter in a very efficient way is described in detail in the following section.

TABLE III

Iteration Steps Needed for the Direct Determination of the Fourth Root of the ArH^+-Matrix without Using Prediagonalization Results[a]

M	$\lambda_k^{(M)}$	$\lvert q_M \rvert$	k
1	−526.0227894	0.5097598	1
2	−526.1026749	0.2222892	1
3	−526.1207424	0.3033201	1
4	−526.1544377	0.1224675	1
5	−526.1635099	0.0477307	1
6	−526.1117487	0.0813802	2
7	−526.1141247	0.0233395	2
8	−526.1144214	0.0074782	2
9	−526.1265023	0.2823006	2
10	−526.1144114	0.0073254	3
11	−526.1144433	0.0028433	3
12	−526.1144478	0.0011203	3
13	−526.1144479	0.0004486	3
14	−526.1644969	0.0069209	3
15	−526.1144478	0.0000437	4
16	−526.1144478	0.0000175	4
17	−526.1144478	0.0000042	4
18	−526.1144478	0.0000012	4
19	−526.1144478	0.0000003	4

[a] Nonzero coefficients of the starting vector: $1/\sqrt{2}$ and $-1/\sqrt{2}$ in those positions which are to be dominant.

Notation: see TABLE I. Resulting exact values of the expected dominant coefficients of the eigenvector: 0.666712; −0.465193. Other important components: 0.374336; −0.103378; 0.374345; −0.103378.

3. Root-Homing Procedure (RHP)

For the calculation of K roots one needs as input K qualitative trial vectors $\mathbf{b}_j^T$ ($j = 1,..., K$) which contain rough approximations for the dominant coefficients of the desired vectors. They can be found by inspection, for instance from simple MO-theory, or by solving a very small CI problem considering only main configurations.

Then a prediagonalization of the matrix **A** is carried out. That is, a submatrix $\mathbf{A}_{\text{sub}}$ of small order is diagonalized which consists of matrix elements of **A** between main configurations and a given number of configurations which have according to any selection criterion the strongest interactions with the main configurations [3]. One assigns to each trial vector $\mathbf{b}_i^T$ $(i = 1,..., K)$ one prediagonalization vector $\mathbf{b}_j^{(0)}$ which has the largest overlap with the latter (one-to-one correspondence). The numbers of these so selected vectors $\mathbf{b}_j^{(0)}$ are called $\nu_1, \nu_2, ..., \nu_K$. Since the $\mathbf{b}_{\nu_1}^{(0)}, ..., \mathbf{b}_{\nu_K}^{(0)}$ are energetically ordered the $\nu_1, ..., \nu_K$ are the desired eigenvalue numbers with respect to the zero-order subspace. Its dimension is chosen as $l \geqslant$ maximum $(\{\nu_i\})$ to guarantee that the vector space spanned by the selected prediagonalization vectors is conserved during the iteration procedure. Thus the zero-order subspace consists of the first l prediagonalization vectors filled up by zero coefficients to the dimension of the full secular equation.

It is reasonable to initiate the whole procedure with the calculation of that eigenvalue whose eigenvector structure corresponds to that $\mathbf{b}_j^{(0)}$ which belongs to the lowest eigenvalue of the prediagonalization problem, that is, to start with the eigenvalue number $k =$ minimum $(\{\nu_i\})$: firstly, the lowest eigenvalue obtained in the prediagonalization corresponds in many cases to the lowest eigenvalue of the full equation. Then rearrangements in the subspace do not slow down congence of the eigenvalue treated. Secondly, experience shows (see Section 5) that rearrangements of other roots still to be calculated often take place in the subspace related to $(\tilde{a}_{ij})$ already during the iterations for the root just treated which avoids again slowdown of the convergence when the next root is calculated. In addition, when proceeding on that way the chance becomes very high to fill up all possibly existing eigenvalue holes between the calculated roots with approximate values obtained from the diagonalization of $(\tilde{a}_{ij})$.

The procedure which enforces convergence to an eigenvector with a given set of dominant components runs as follows: from all M eigenvectors of the matrix $(\tilde{a}_{ij})$ the desired one is that which gives the greatest weight in the expansion (1) to that prediagonalization vector which represents the structure of the eigenvector wanted. Hence, in our modified scheme the eigenvector matrix $(\alpha_{i,j}^{(M)})$ is inspected after each iteration step: if it is found that now $\alpha_{\tilde{k}}^{(M)}$ instead of $\alpha_k^{(M)}$ has the largest contribution from that prediagonalization vector then the following iteration $(M \to M + 1)$ is carried out after changing k to $\tilde{k}$. Such exchanges will occur until convergence to the desired eigenvector begins.

The calculation of further eigenvectors and eigenvalues is carried out in an analogous manner: it is determined by the same method which of the remaining eigenvectors of the $(\tilde{a}_{ij})$ matrix obtained in the last iteration for the eigenvector just treated represent the structures of the eigenvectors being sought, i.e. that or those already determined and all remaining species still to be treated. One gets

a new set of numbers $\{\tilde{\nu}_r\}$, chooses again $l \geqslant$ maximum $(\{\tilde{\nu}_r\})$ and uses as basis vectors the l eigenvectors of $(\tilde{a}_{ij})$ which provide, in general, an improved zero-order subspace. That procedure takes also care of the possibility that the eigenvalue numbers of roots already obtained might change while treating the other vectors.

$k =$ minimum$'(\{\tilde{\nu}_{r'}\})$ is taken again as the eigenvalue number at the beginning of the calculation of the following root where the prime at the index r means that the eigenvalue just calculated is to be excluded.

The modified procedure is outlined in the following scheme:

A. Supply K trial vectors $\mathbf{b}_i^T$ $(i = 1, 2,..., K)$ which show the qualitative structure of the dominant components of the desired full vectors.

B. Carry out a prediagonalization of order n with resulting vectors $\mathbf{b}_j^{(0)}$, $j = 1, 2,..., n$.

C. Assign to each $\mathbf{b}_i^T$ by an overlap test a corresponding partner in the $\mathbf{b}_j^{(0)}$ space (one-to-one correspondence). The numbering of the selected $\mathbf{b}_j^{(0)}$ vectors be $\{\nu_r\}$; $r = 1, 2,..., K$.

D. Choose the dimension of the zero-order subspace as

$$l \geqslant \text{maximum}(\{\nu_r\})$$

and start the procedure with that root which has the number (in the subspace)

$$k' = \text{minimum}(\{\nu_r\}).$$

Set $M = l$, $k = k'$

E. Form the $M \times M$ matrix $(\tilde{a}_{ij})$ and do one Davidson iteration on the kth root $\lambda_k^{(M)}$ of $(\tilde{a}_{ij})$. When convergence is achieved continue at H.

F. Inspect the eigenvector matrix $(\alpha_{i,j}^{(M)})$ to find that vector with the number $\tilde{k}$ which among all M eigenvectors contains in its expansion (1) the subspace vector $\mathbf{b}_k^{(0)}$ with the highest absolute weight.

G. Set $k = \tilde{k}$, $M = M + 1$, continue at E.

H. Compute the eigenvector with formula (1) by using for M and k their values in the last iteration step. The desired root is $\lambda_k^{(M)}$.

I. If another case is to be treated find (in the same way as in F.) the possible new labelling for the roots already solved as well as for those still to be treated which is called $\{\tilde{\nu}_r\}$; $r = 1, 2,..., K$ (with respect to the eigenvector space of the last iteration step).

Choose the new subspace dimension l as

$$l \geqslant \text{maximum}(\{\tilde{\nu}_r\}).$$

The new zero-order subspace is formed by the vectors

$$\mathbf{b}_j^{(0)} = \mathbf{x}_j^{(M)} \qquad j = 1, 2,..., l \text{ (Formula (1))}$$

The next root to be treated is

$$k' = \text{minimum}(\{\tilde{\nu}_r\} - \{\tilde{\nu}_r\}_{\text{already treated}}).$$

Set $k = k'$; $M = l$; $\nu_r = \tilde{\nu}_r$, $r = 1, 2,..., K$. Continue at E.

With the help of this procedure not only the starting points for the roots still to be treated are improved indirectly by carrying out the iterations for one root but also the "control vectors" $\mathbf{b}_{k'}^{(0)}$ get closer to the desired eigenvectors each time when a further root is obtained.

According to C. any trial vector $\mathbf{b}_i^T$ will find a partner in the $\mathbf{b}_j^{(0)}$ space. But a badly chosen prediagonalization might not provide at all an appropriate partner vector for $\mathbf{b}_i^T$ or lead to a loss of the one-to-one correspondence. Thus it is useful to introduce in addition a threshold (to be established by experience) which acts as a lower bound for the allowed overlaps. In the case that a guess vector $\mathbf{b}_i^T$ fails to exceed this threshold, $\mathbf{b}_i^T$ itself can be considered as zero-order trial vector and, after orthonormalization, can be taken to generate the zero-order subspace. If the full problem has no solution with the expected structure this will lead, of course, to a breakdown of the method.

4. Convergence

In order to get an idea about the convergence behavior of Davidson's procedure we consider the following simplified situation: first the present consideration is restricted to the lowest root, secondly the zero-order subspace is assumed to consist of one unit vector with only one nonzero component (this situation is realistic if this component corresponds to the Hartree–Fock determinant) which is assumed without loss of generality to hold position 1.

The first iteration generates $\mathbf{b}_2{}^1$ according to Eq. (2) Section 2.

$$\mathbf{b}_2{}^1 = \mathbf{d}_2 / |\, \mathbf{d}_2 \,|^{1/2}$$

$$\mathbf{d}_2 = \left\{0, \frac{A_{12}}{A_{11} - A_{22}}, \frac{A_{13}}{A_{11} - A_{33}}, ..., \frac{A_{1N}}{A_{11} - A_{NN}}\right\} \tag{3}$$

which is orthogonal to $\mathbf{b}_1^{(0)}$. (The 0/0 situation arising for the first component is solved by setting this quotient equal to zero.)

The two by two matrix $(\tilde{a}_{ij})$ has then the following elements:

$$\tilde{a}_{11} = A_{11}$$

$$\tilde{a}_{12} = \tilde{a}_{21} = \frac{1}{|\,\mathbf{d}_2\,|^{1,2}} \sum_{k=2}^{N} \frac{A_{1k}^2}{A_{11} - A_{kk}} \tag{4}$$

$$\tilde{a}_{22} = \frac{1}{|\,\mathbf{d}_2\,|} \sum_{i=2}^{N} \sum_{k=2}^{N} \frac{A_{1i}}{A_{11} - A_{ii}} A_{ik} \frac{A_{1k}}{A_{11} - A_{kk}} \tag{5}$$

Its eigenvalues are

$$\lambda_{1,2} = \tfrac{1}{2}\{\tilde{a}_{11} + \tilde{a}_{22} \pm (\tilde{a}_{11} - \tilde{a}_{22}) \cdot \sqrt{1 + (4\tilde{a}_{12}^2/(\tilde{a}_{11} - \tilde{a}_{22})^2)}\}$$

Since $|\,\lambda_1 - \tilde{a}_{11}\,|$ is small compared to $|\,\tilde{a}_{11}\,|$, the argument of the square root has to be close to unity and, hence, expanding the square root up to the first order yields for the lower root

$$\lambda_1 \approx \tilde{a}_{11} + \frac{\tilde{a}_{12}^2}{\tilde{a}_{11} - \tilde{a}_{22}}\,.$$

Inspection of the Eqs. (3) to (5) shows that the first Davidson iteration is equivalent to a variational superposition of the zero and first-order wavefunctions (corresponding to $\mathbf{b}_1^{(0)}$ and $\mathbf{b}_2{}^1$ respectively) obtained by a perturbation treatment of the Hamilton matrix considering the off-diagonal elements as perturbation. Hence the lowering of $\tilde{a}_{11}$ can be expressed in terms of zero (E_0), second (E_2) and third (E_3) order perturbation energies, respectively, as

$$\lambda_1 - \tilde{a}_{11} = \frac{E_2{}^2}{|\,\mathbf{d}_2\,| \cdot E_0 - E_3}$$

That means that the Davidson scheme converges already in the first iteration step better than does a first order perturbation treatment and that the energy improvement is better than the perturbational correction in third order.

Good convergence requires that the off-diagonal elements are small compared to the separations of the diagonal elements (see Eq. (3)).

An investigation of the convergence behavior in the further iteration steps and its relationship to perturbation schemes is in progress which is expected to explain the good convergence in case of near-degenerate roots.

5. Results and Applications

The RHP is applied to two CI-matrices of the molecule C_2H_6 and ArH^+ with dimension $N = 3316$ and $N = 905$, respectively. In the C_2H_6 case qualitative trial vectors $\mathbf{b}_i{}^T$ for three desired states are supplied whose partner vectors $\mathbf{b}_j^{(0)}$

in the zero-order subspace resulting from a prediagonalization of order 20 have the numbers 1, 4 and 7. The corresponding roots of the full secular equation come out having the eigenvalues numbers 1, 2, and 6.

This case provides an example for the phenomenon which is generally discussed in Section 3: while iterating on the first root a rearrangement of the subspace takes place which allows to do the next root with the right k value for all iterations. The third state, however, has after completion of the second root still not its final eigenvalue label. This fluctuation of the highest root could eventually be avoided if instead of choosing the minimal dimension of the subspace $l = \text{maximum}(\{\nu_r\})$ (see Steps D and I of the scheme in Section 3) a greater l value would be taken.

In a further test the sixth root of the full equation is calculated directly without carrying out any prediagonalization. Here the trial vector $\mathbf{b}_1{}^T$ which consists of a 1.0 in the position of the dominant configuration and of zeros for the remaining components is chosen to form the zero-order subspace of dimension 1. Table I shows how the method starting from $k = 1$ successively identifies higher k values as the desired ones. A change of the root number is, in general, accompagnied by an increase of the absolute value of the error vector $\mathbf{q}_M$.

In addition, one sees from Table I that a reduced accuracy requirement allows to get a higher root without filling up all lower eigenvalue holes in the $(\tilde{a}_{ij})$ space. This gives hope to find even rather high-lying roots without too much effort.

In Table II it is demonstrated that the lower dummy roots which are generated as by-products in the iteration process shown in Table I provide rather good approximations for the actual lower roots which are determined by the unmodified Davidson method. No convergence difficulties arise from the near-degeneracy of the roots with numbers 4 and 5 (13 iterations for the fourth and only 8 iterations for the fifth using as convergence test $|\mathbf{q}_M| < 10^{-6}$).

Table III shows in analogy to Table I the results of a direct determination of the actual 4th root of the ArH^+ case using only the qualitative guess vector as zero-order space. In order to test the power of the RHP in worse situations the nonzero components of $\mathbf{b}_1{}^T = \mathbf{b}_1^{(0)}$ were chosen to consist of only $1/\sqrt{2}$ and $-1/\sqrt{2}$ in the positions of the two dominant configurations. Despite strong mixing of other components the eigenvector with number 4 in the full secular equation which of all computed lower states resembles the given trial vector most is successfully identified by the procedure. By carrying out prediagonalizations in both cases the desired roots are found, of course, with less iterations.

The RHP turns also out to be very effective method for the energy extrapolation technique suggested by Buenker and Peyerimhoff[4]. This method tries to predict the eigenvalues of the matrix of a full CI which is too big to be treated, in the following way: one solves a series of secular equations of manageable size corresponding to different lengths of the wavefunction expansion. The resulting sets

of eigenvalues are used to find approximations for the roots of the full CI by an extrapolation scheme. Because of technical reasons one treats the largest secular equation corresponding to the longest expansion first and continues with equations of descending order.

As long as several successive eigenvalues are wanted and as long as these roots have the same ordering in all secular equations to be treated this task can easily be solved by the use of the MOR method: The truncated eigenvectors of one eigenvalue problem form very good starting vectors for the following reduced one.

If this is to be carried out for a single higher-lying root or for several non-successive roots the unmodified Davidson scheme can be used if the ordering of the roots is maintained in all secular equations to be treated. The truncated reorthogonalized eigenvectors of one secular equation solved are used as to form the zero-order subspace for the solution of the next secular equation which leads to a very fast convergence.

But, in general, only the RHP is successful in yielding the results needed for the extrapolation procedure since in many cases the desired roots, especially higher-lying ones, have a different eigenvalue numbering in the series of eigenvalue equations to be solved.

That situation arises, for instance, in the case of the 6th root of the C_2H_6 problem as shown in Table IV. The eigenvector of that root changes completely its structure

TABLE IV

Comparison of the Dominant Eigenvector Components Resulting from Davidson's Method and the RHP Applied to a Series of C_2H_6 CI Matrices[a]

Dimension	3316		2698		2048		1656	
Method	A	B	A	B	A	B	A	B
Root number	6	6	6	6	6	7	6	7
Dominant	0.9390	0.9390	0.9401	0.9401	—	0.9481	—	0.9538
eigenvector	0.0574	0.0574	0.0580	0.0580	—	0.0633	—	0.0709
components	−0.1226	−0.1226	−0.1252	−0.1252	—	−0.0932	—	−0.0675
	0.0578	0.0578	0.0592	0.0592	—	0.0624	—	0.0669
	−0.1229	−0.1229	−0.1252	−0.1252	—	−0.0931	—	−0.0675
	0.0578	0.0578	0.0592	0.0592	—	0.0624	—	0.0670
	—	—	—	—	0.9833	—	0.9848	—
	—	—	—	—	−0.1265	—	−0.1405	—

[a] A, vectors obtained with Davidson's method; B, vectors obtained with RHP. Only coefficients with an absolute value greater than 0.05 are listed; — indicates coefficients in corresponding positions with an absolute value less than 0.05.

when one proceeds from the second to the third secular equation of the series. An inversion of the roots with numbers 6 and 7 occurs when going from dimension 2698 to 2048 and hence the unmodified Davidson method leads to a state not wanted (see columns A in Table IV). The RHP, on the other hand, automatically changes the eigenvalue number (k value, see Section 3, steps F and G of the scheme) and yields the root with the right eigenvector in all cases (see columns B in Table IV).

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